KINETICS OF COAL LIQUEFACTION

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INTRODUCTION

Information on the rates of coal dissolution which is needed in the design of reactors in a coal liquefaction plant has been very limited; therefore, methods are needed by which dissolution rate data can be extrapolated to other operation conditions. In this section, the rates of solvation of coal in various oils under hydrogen pressure without the presence of catalyst are examined.

The role of solvents in coal liquefactions has been discussed by Oele et al[1]. Anthracene oil, for example, is a good solvent when used at a high temperature about 700°K; and the solvent itself can be recovered from the solution substantially unchanged. The action of solvent is presumed to facilitate thermal degradation of coal causing breakage of the coal into smaller and more readily dissolvable fragments. In recent years, many investigators[2, 3, 4, 5] have postulated that in the liquefaction process the hydrogen added to the coal is largely derived from the vehicle solvent such as recycle oil, anthracene oil or partly hydrogenated phenanthene. The function of hydrogen and catalyst is to subsequently re-hydrogenate the vehicle solvent. Once a part of the coal has been brought into the solution by physical dissolution or by partial hydrogenation, the molecular species derived from the coal can migrate in the solution where it can be further hydrogenated.

Curran et al[2] studied the kinetics of the transfer of hydrogen from tetralin to bituminous coal and coal extracts. They proposed that the dissolution is a first order reaction, and assumes that thermal decomposition of coal into free radical components occurs with the slowest characteristic rate constant. Klopper et al[4] noted a marked increase on coal dissolution as the partial pressure of hydrogen was increased in a batch autoclave system.

In this study a rate equation for dissolution of coal under hydrogen pressure is proposed which can describe fairly closely the experimental data reported by Pittsburg & Midway Coal Mining Company[6] and the University of Utah[7]. Data obtained by Colorado School of Mines[8] are used to compare the sulfur content in desulfurized coal.

University of Utah Coal Hydrogenation

The data on coal hydrosolvation, without catalyst, from the University of Utah are examined in this study .
    Coal was slurried in a coal derived oil and was hydrotreated under hydrogen pressure in a batch stirred tank reactor. Experiments were performed in a temperature range of 400-500°C, under a hydrogen pressure of 0-2000 psig with a residence time ranging from 2 to 30 minutes.

Analysis of the coal used is shown in Table 1. Examining the data reported, an empirical rate equation is proposed here which seems to represent the dissolution rates closely. The proposed rate expression has the form:

$$\begin{bmatrix} \text{rate of} \\ \text{dissolution} \end{bmatrix} = \begin{bmatrix} \text{rate} \\ \text{constant} \end{bmatrix} \bullet \begin{bmatrix} \text{fraction of undissolved} \\ \text{solid organics} \end{bmatrix} \bullet \begin{bmatrix} \text{coal-solvent} \\ \text{ratio} \end{bmatrix}$$

or $\qquad r_A = k(C_{SO})(1-X)(\frac{C}{S}) \qquad\qquad X < 0.95 \qquad\qquad (1)$

where r_A is the rate of dissolution in gm. per. hr. c.c. reactor volume,

$\quad C_{SO}$ is the weight fraction of organics in the untreated coal,

$\quad\quad k$ is the dissolution rate constant in gm. per. hr. per c.c. reactor volume

$\quad\quad X$ is the conversion, defined as (amount of solid organics dissolved)/ (amount of solid organics in the untreated coal),

and $\quad \frac{C}{S}$ is the coal to solvent (weight) ratio.

Integrating Equation (1) gives:

$\qquad \ln(1-X) = -k \cdot \theta \qquad\qquad\qquad\qquad\qquad\qquad (2)$

where θ for the batch reactor is defined as $(C_{SO})(\frac{t}{C_{ao}})(\frac{C}{S})$,

$\quad\quad t$ is the reactor time in hours,

and $\quad C_{ao}$ is grams of ash free coal per c.c. of reactor volume. The value of C_{ao} is estimated to be 0.245 gm/c.c. for the Utah experiments.

The University of Utah's data are shown in Figure 1 in terms of $\ln(1-X)$ and θ as suggested by the above equation. Three hydrogen pressure levels were investigated and the effect of pressure on the dissolution rate constant, k, is shown in Figure 2. This figure suggests an exponential dependency of the rate constant of the hydrogen partial pressure. Incorporating the hydrogen pressure effect on the rate constant, and assuming an Arrhenius temperature dependency, the rate equation given by Equation (1) takes the form

$\qquad r_A = k_o EXP(-E/RT) \; exp(0.000684 \; P_{H_2})(C_{SO})(1-X)(\frac{C}{S}) \qquad\qquad (3)$

where the dissolution rate constant, k, in Equation (1) and (2) is assumed to have the form $k = k_o exp(-E/RT) \; exp(\beta P_{H_2})$ and P_{H_2} is the partial pressure of hydrogen in psia.

The University of Utah's experimental data are then shown in Figure 3 plotted in the form suggested by Equation (2) and taking into account the hydrogen pressure dependency of the dissolution rate constant. In Figure 4 the temperature dependency of the dissolution rate constant is assumed, and the activation energy is found from the Arrhenius plot (given in Figure 5) to be about 11 Kcal/mole. Calculated conversions using the above activation energy are compared with experimentally reported conversions in Figure 6. It can be seen from this figure that the agreement is good.

Solvent Refined Coal (SRC) Process

The experimental data for the SRC process are taken from Pittsburg and Midway's monthly reports[6]. Raw coal was pulverized to -150 mesh and mixed with solvent (Table 2 gives the analysis of the coal used). The coal-solvent slurry was pumped together with hydrogen, through a preheat coil (an 18 foot length of high pressure tubing having 13/64 inch I.D.) to a reactor zone or "dissolver coil" (length to diameter ratio = 10:1). The dissolver was operated in a temperature range of 375-450°C and a pressure range of 1500-2000 psig, (a majority of the experiments were run at 1500 psig). The starting solvents for the experiments were carbon black feedstock (FS120) and anthracene type solvent.

Two modes of operation were studied: recycle and the single-Throughput mode. The recycle stream consisted of either unfiltered coal solution, or a mixture of unfiltered coal solution and distilled liquid product. The single throughput operation used the distilled liquid product from the previous experimental run as the solvent feed for the next run.

The performance equation for the plug flow reactor used in the SRC experiments is similar to the performance equations for a batch reactor used by the University of Utah given by Equation (2) if the quantity θ is redefined.

For the plug-flow reactor and single throughput operation Equation (2) becomes

$$\ln(1-X) = -k \cdot \theta' \qquad (4)$$

For the plug-flow reactor and the recycle mode operation integration of Equation (1) gives

$$\ln\left(\frac{1-X_2}{1-X_1}\right) = -k \cdot \theta' \qquad (5)$$

where $\theta' = \left(\frac{V}{F}\right)\left(\frac{C}{S}\right)(C_{SO})$ is in hr.-c.c./gm., V is the volume of the reactor

in c.c., F is the mass flow rate of solid organics into reactor in gm. per hr., and X_1, X_2 are conversions at the entry and exit of a recycle reactor.

Based on Pittsburgh and Midway's data $\ln(1-X)$ or $\ln\left((1-X_2)/(1-X_1)\right)$ was plotted as a function of θ', as shown in Figure 7. The slope of the line through the data represents the value of $(-k)$. Assuming on Arrhenius dependency of the dissolution rate constant, k, on temperature (i.e., $k \alpha \exp(-E/RT)$, the slope of the curve of $\ln k$ versus $1/T$ (see in Figure 9) is equal to $(-E/R)$. The value of the activation energy, E, is found to be 4.5 Kcal/mole with $k_0 = 15.34$ gm/hr.-c.c. In calculating k_0 the same dependence of the dissolution rate on the partial pressure of hydrogen that was observed for University of Utah's experiments was assumed for the Pittsburgh and Midway's experiments. This is a tentative assumption which must be varified by further experiments.

The small activation energy suggests that the rate of dissolution is probably controlled by the counter-diffusion of dissolved organic components from coal to solvent and the dissolved hydrogen in the solvent to the coal particle. Using the above value of the activation energy and the proposed rate expression conversions are calculated and compared with the experimental values reported by Pittsburgh and Midway as shown in Figure 9. Fairly good agreement between the two can be seen.

Colorado School of Mine Sulfur Removal Experiments

Colorado School of Mines performed a factorial experimental design on desulfurization of coal. Although, their experiments were not intented for kinetic studies of coal dissolution, the relation between the percent sulfur in desulfurized coal and total sulfur content of feed can be compared with that of Pittsburgh & Midway Co. as shown in Figure 11. It can be noted that the anthracene oil curve obtained from their experiments agrees closely with that of runs obtained by Pittsburgh & Midway Co. also from anthracene type solvent.

Discussion

The activation energy for diffusion of a non-polar chemical species in coal derived liquid can be estimated to be 4.3 to 6.0 kcal/gmole which is approximately in the range of the activation energy observed in the University of Utah's and Pittsburgh and Midway's coal dissolution experiments. Thus, it seems reasonable that the dissolution of coal in solvent-hydrogen mixtures may be diffusion controlled.

The rate of coal dissolution appears to be independent of the coal particle size distribution within the range of operating conditions considered. There is evidence[3] that liquefaction process is not a steady erosion of a coal particle, from the outside, but rathe the solvent penetrates the particle pores causing swelling and disintegration of the particles, exposing new surface at which dissolution can take place. Apparently for some coals, temperature above 370-390°C, the coal particles appear to puff up like popcorn and disintegrate into smaller fragments.

The linear dependence of the dissolution rate on the coal-solvent ratio, (C/S), is shown in Figure 10, in which the quantity $-\ln(1-X)/[k(V/F)(C_{S0})]$ is shown as a function of (C/S). This linear relation is observed for coal-solvent ratios ranging from 0.2 to 0.6.

Comparison of Figures 1 and 7 reveals that the rate constant from University of Utah's experimental runs is larger than that from Pittsburg and Midway's runs (see also Figure 21). A possible explanation for this difference is that the batch reactor with a stirring device probably had more tubulent contacting between solvent and coal particles (hence, high mass transfer coefficients) than the tubular

reactor of Pittsburgh and Midway experiments. Furthermore, since the University of Utah and Pittsburgh and Midway used different coals factors such as rank of coal, geological history, and mineral content in ash could have affected liquefaction rate. In particular, mineral matter contained in the coal has been thought to catalyze coal dissolution.

In Solvent Refined Coal process and in most continuous coal liquefaction processes, a preheating section is usually required to heat the incoming feed stream of the dissolution reactor. It is possible that partial dissolution of the coal takes place in this section. Therefore, the contribution of the preheaten section in dissolving the coal should be considered in analyzing the dissolution kinetic.

Conclusions

(1) The coal dissolution data obtained from the Pittsburg and Midway Company and the University of Utah have been evaluated based on a proposed dissolution rate equation. The calculated conversions based on the proposed kinetic rate expression agree fairly closely with the experimental conversions reported by the University of Utah's coal hydrogenation experiments and Pittsburg and Midway's SRC experiment. The rate of dissolution for x < 0.95 can be represented by the following empirical equation.

$$r_A = k_0 \exp(-E/RT)(C_{SO})(1-X)\left(\frac{C}{S}\right)\exp(0.000684 \cdot P_{H_2})$$

	Illinois, River King Coal	Kentucky No. 9 Coal
where k_0	2125 gm/hr.-c.c.	15.3 gm/hr.-c.c.
E	11 Kcal/g-mole	4.5 Kcal/g-mole

(2) The temperature effect on the rate constant for both processes has been examined and the activation energies for coal dissolution vary depending on the type of coal and contacting devices used. Based on the small activation energies calculated from experimental data, it is postulated that the rate of dissolution is probably controlled by the diffusion of some organic component from the coal surface into solvent-hydrogen mixture.

(3) The dissolution rate of coal appears to depended exponentially on the hydrogen partial pressure. However, further investigations are needed to validate this conclusion.

(4) A rough relation exists between the precent of sulfur in solid coal fed and the percent of sulfur remaining in desulfurized coal for a given type of solvent.

Acknowledgment

TABLE 1

Analysis of Coal Used in the University of Utah's Coal
Hydrogenation Experiments[7] Illinois, River King Coal.

Proximate	wt.%	Ultimate (maf)	wt.%
Moisture	5.6	Carbon	79.7
Ash	9.9	Hydrogen	5.4
Volatile Matter	36.7	Nitrogen	2.1
Fixed Carbon	47.8	Sulfur	3.8
	100.0	Oxygen (diff.)	9.0
			100.0

TABLE 2

Analysis of Coal Used in the SRC Process[6] Kentucky No. 9 Coal

Proximate	wt.%		Ultimate	wt.% (dry)	
Moisture	3.90	9.34	Carbon	70.56	72.76
Ash	11.33	8.40	Hydrogen	4.87	5.24
Volatile Matter	36.35	35.28	Nitrogen	1.48	1.63
Fixed Carbon	48.42	46.98	Chlorine	.07	.10
	100.00	100.00	Sulfur	4.27	3.35
			Ash	11.79	9.27
			Oxygen (diff)	6.96	7.65
				100.00	100.00

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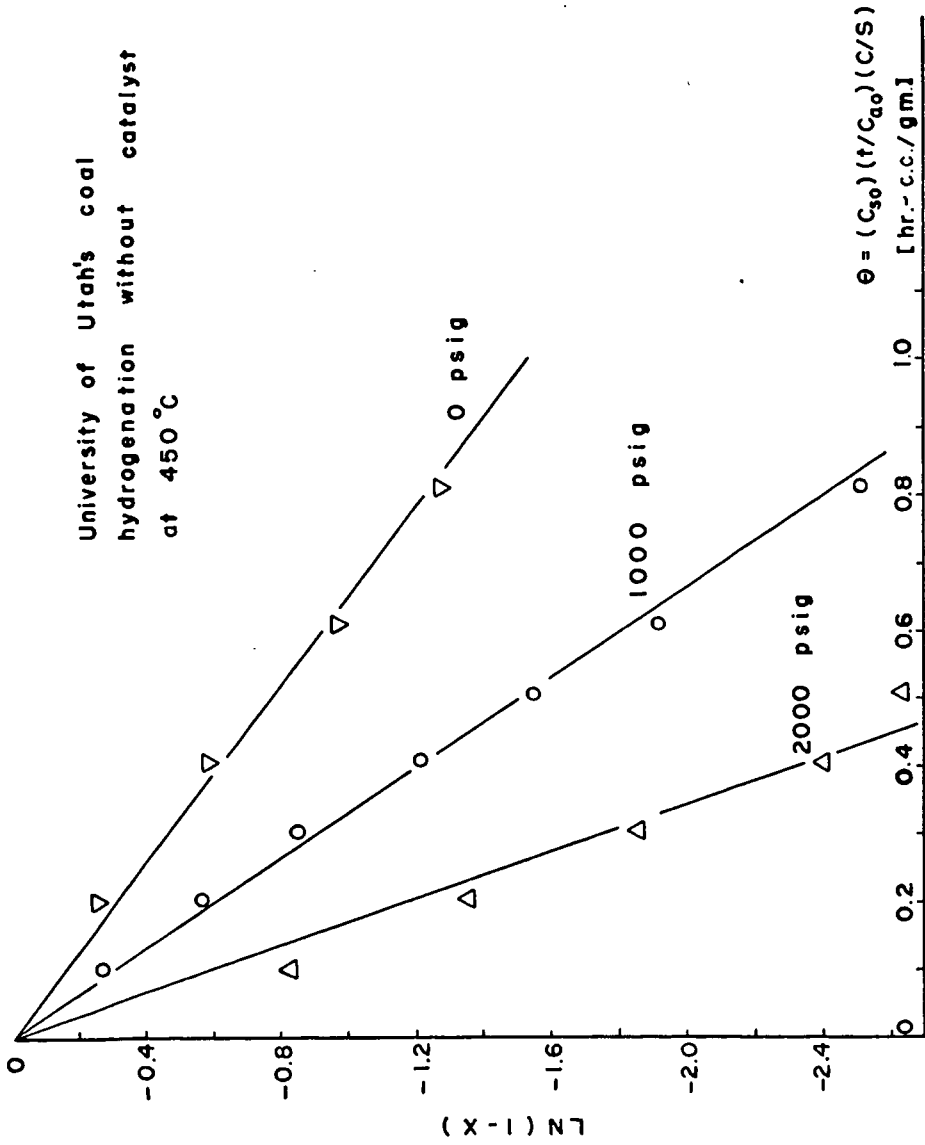   Contract No. 14-32-0001-1225 (May 1973).

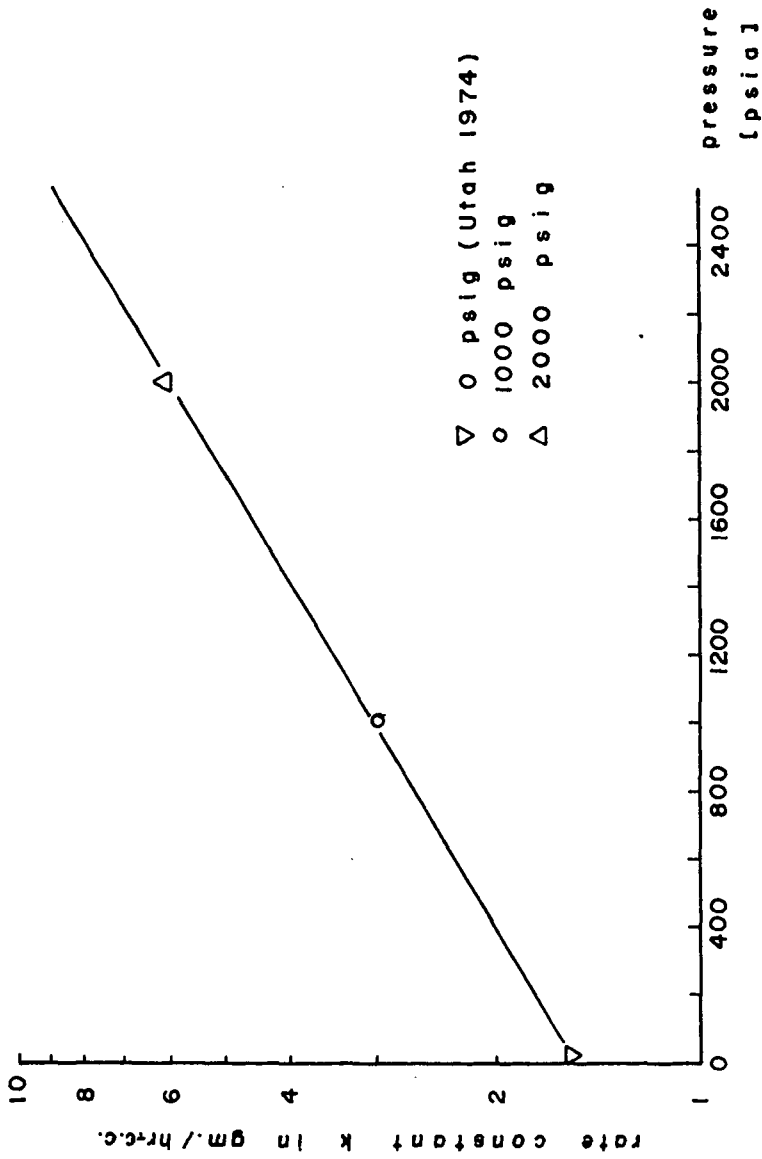Figure 1   EFFECT OF HYDROGEN PARTIAL PRESSURE ON RATE CONSTANT.

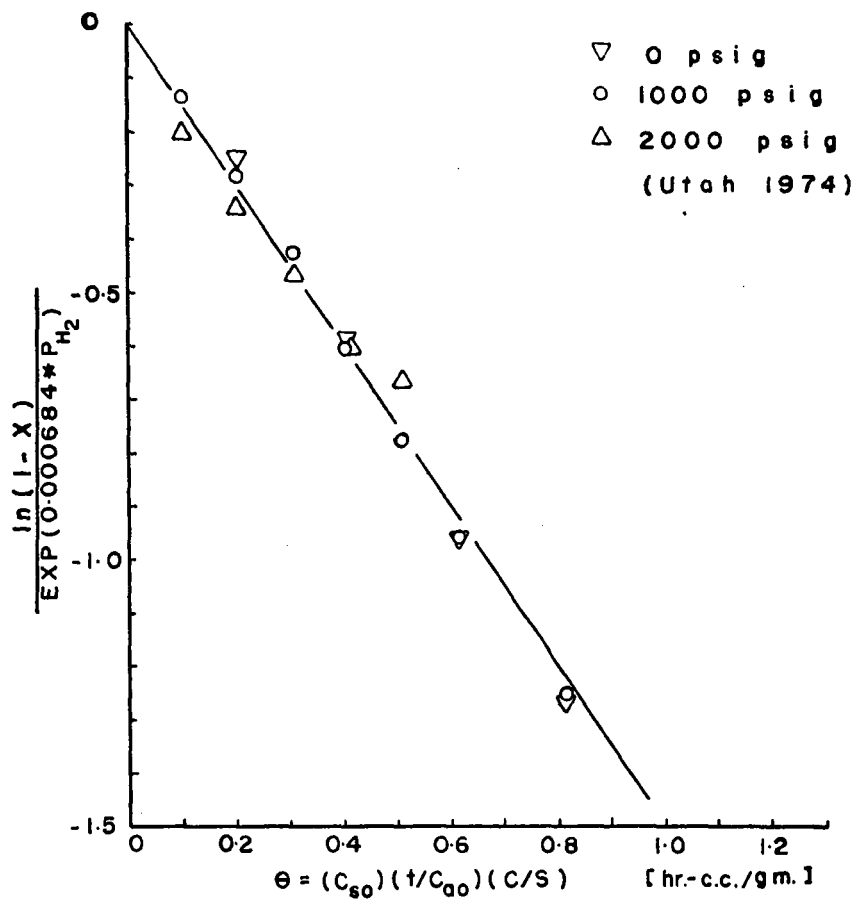Figure 2 PRESSURE EFFECT ON RATE CONSTANT (Temp. = 450°C)

Figure 3 CORRELATION OF KINETIC RATE EQUATION ON COAL DISSOLUTION
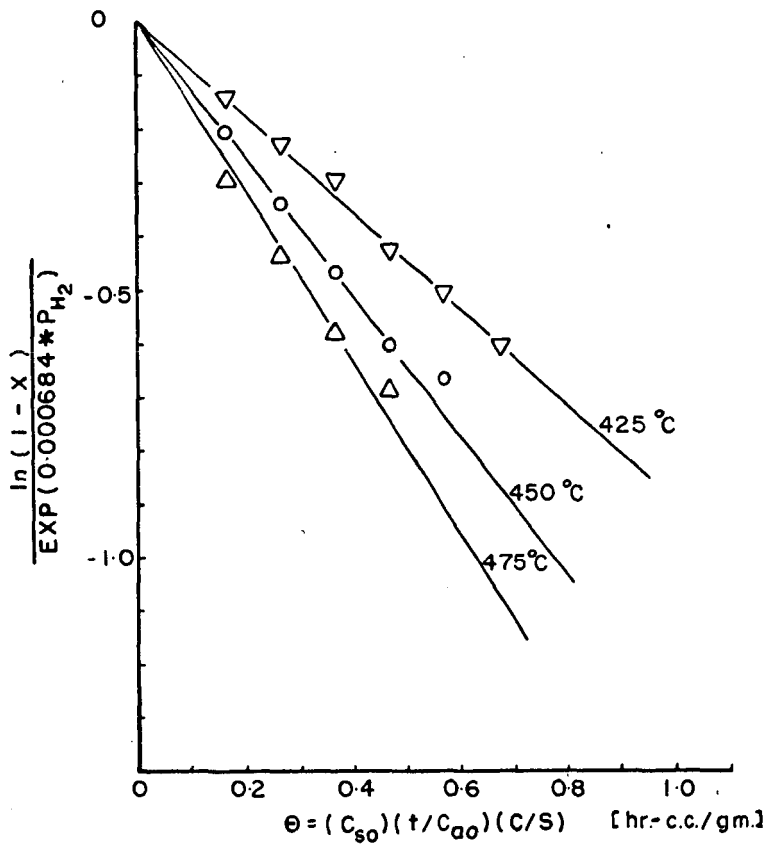(Temp. = 450°C)

Figure 4   TEMPERATURE EFFECT ON RATE CONSTANT OF COAL DISSOLUTION
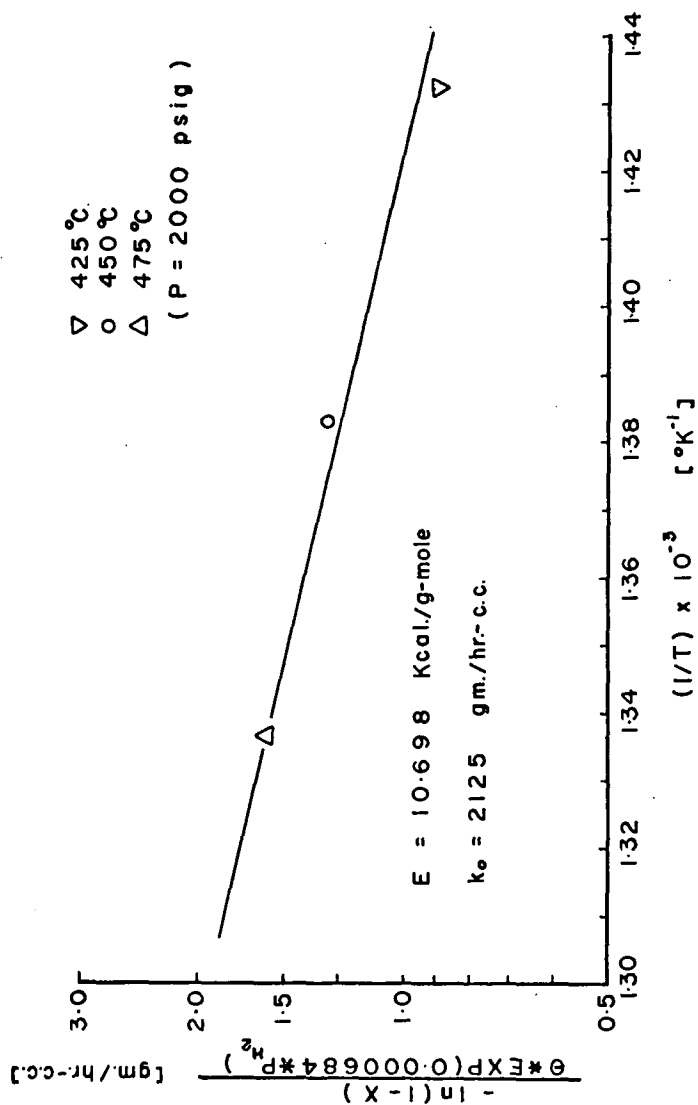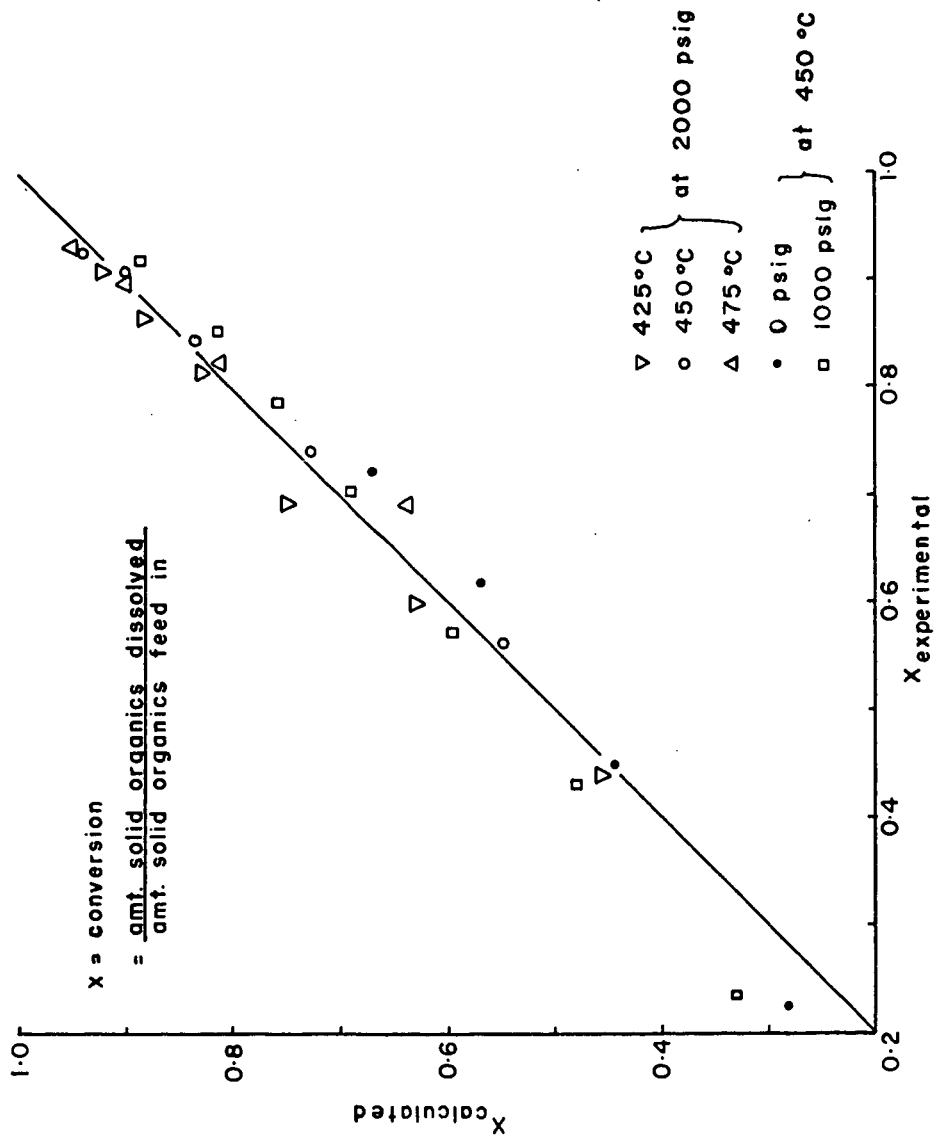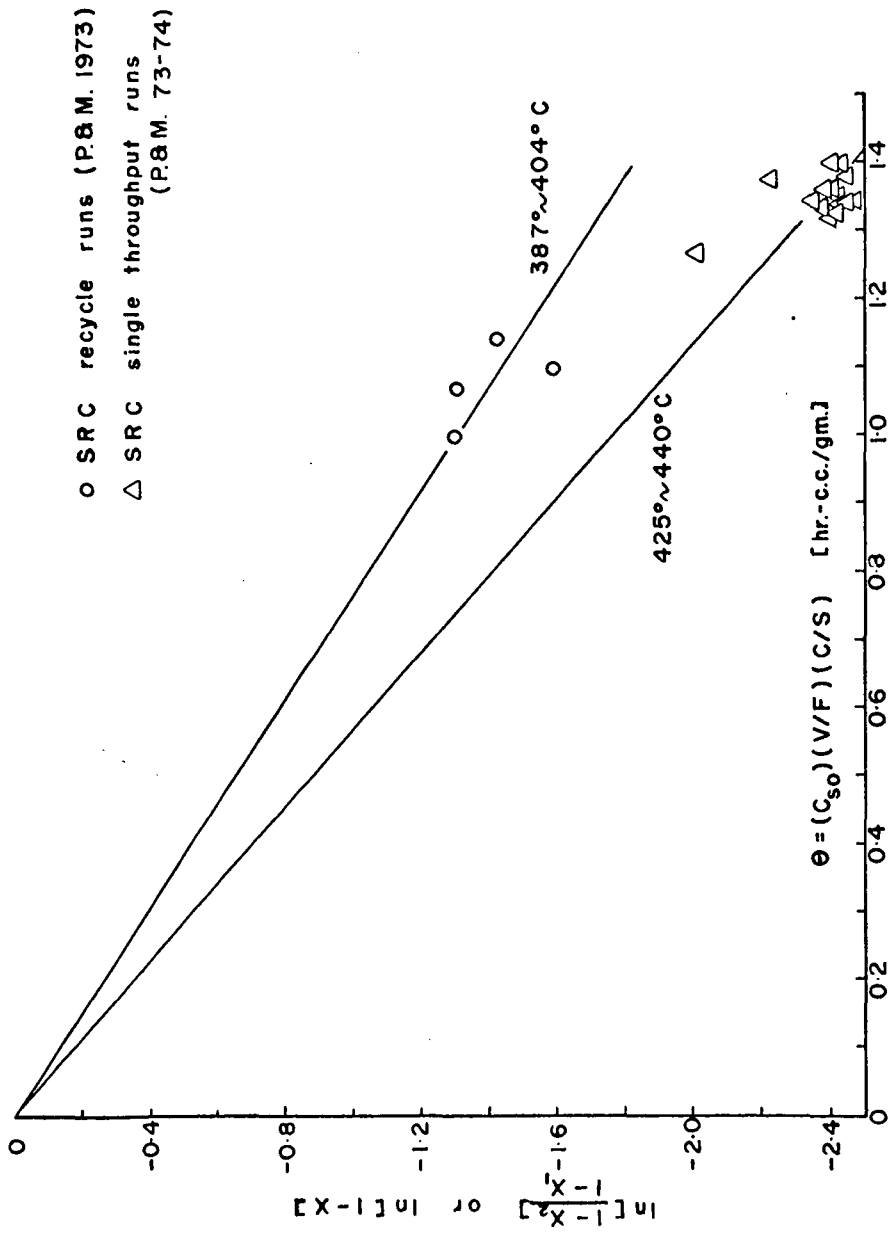(without catalyst)

Figure 5 ARRHENIUS' PLOT FOR UNIVERSITY OF UTAH'S COAL HYDROGENATION EXPERIMENT (without catalyst)

Figure 6 COMPARISON OF CALCULATED AND EXPERIMENTAL CONVERSION FROM UNIVERSITY OF UTAH'S COAL
HYDROGENATION (without catalyst)
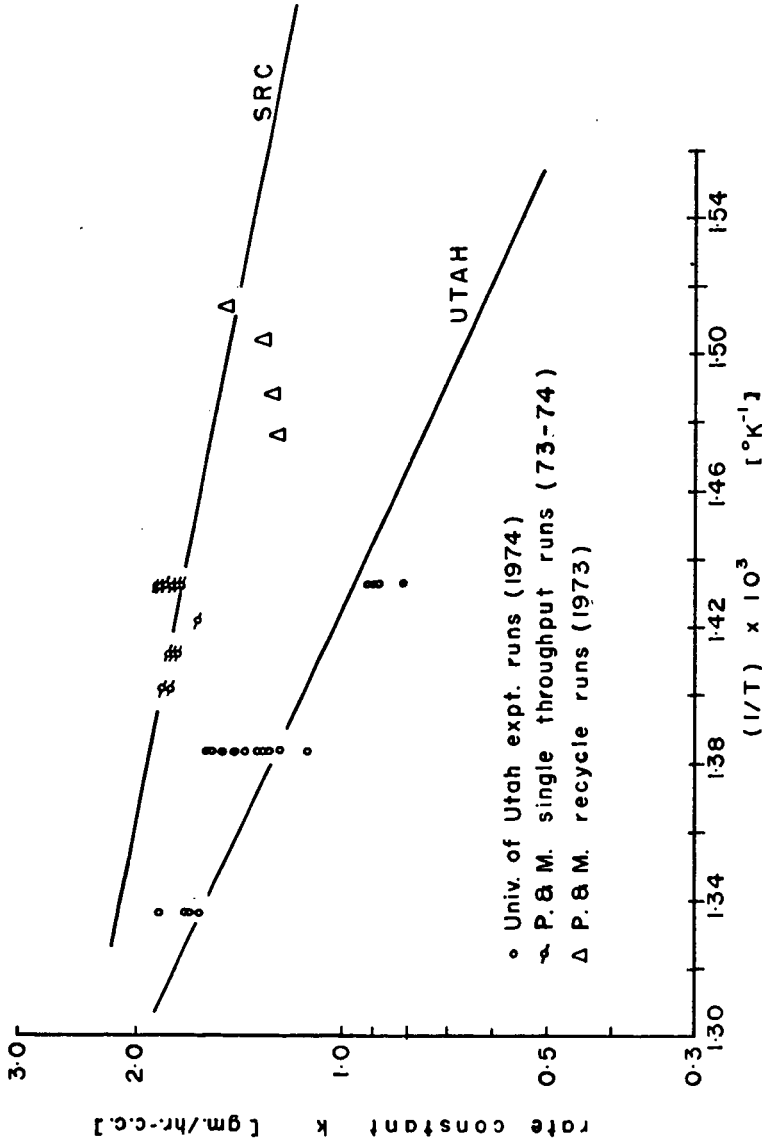
Figure 7 PLOT OF ln(1-X) vs. θ TO EVALUATE RATE CONSTANT.

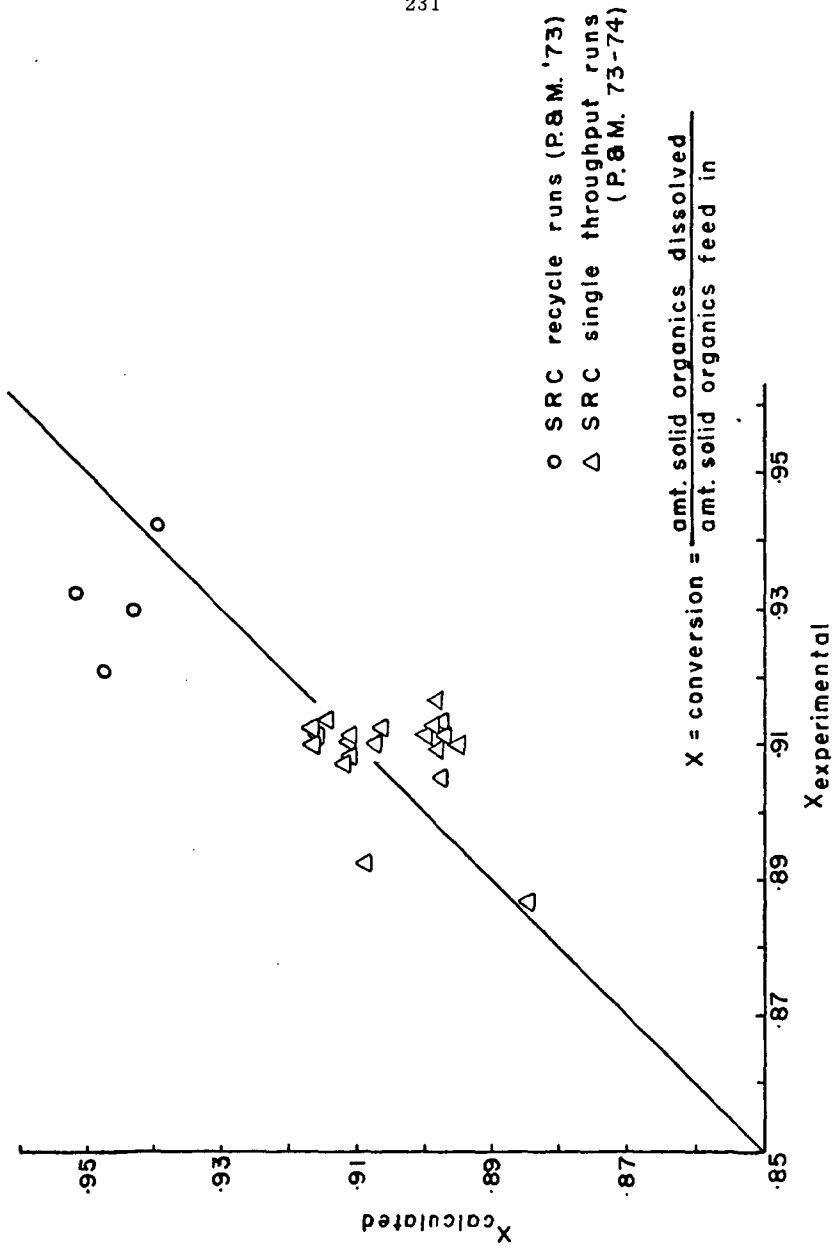Figure 8   COMPARISON OF ARRHENIUS' PLOT FOR PITTSBURG & MIDWAY COMPANY DATA AND UNIVERSITY OF UTAH EXPERIMENTAL RUNS.

o S R C recycle runs (P.& M. '73)

△ S R C single throughput runs
(P.& M. 73-74)

$$X = \text{conversion} = \frac{\text{amt. solid organics dissolved}}{\text{amt. solid organics feed in}}$$

$X_{experimental}$

$X_{calculated}$

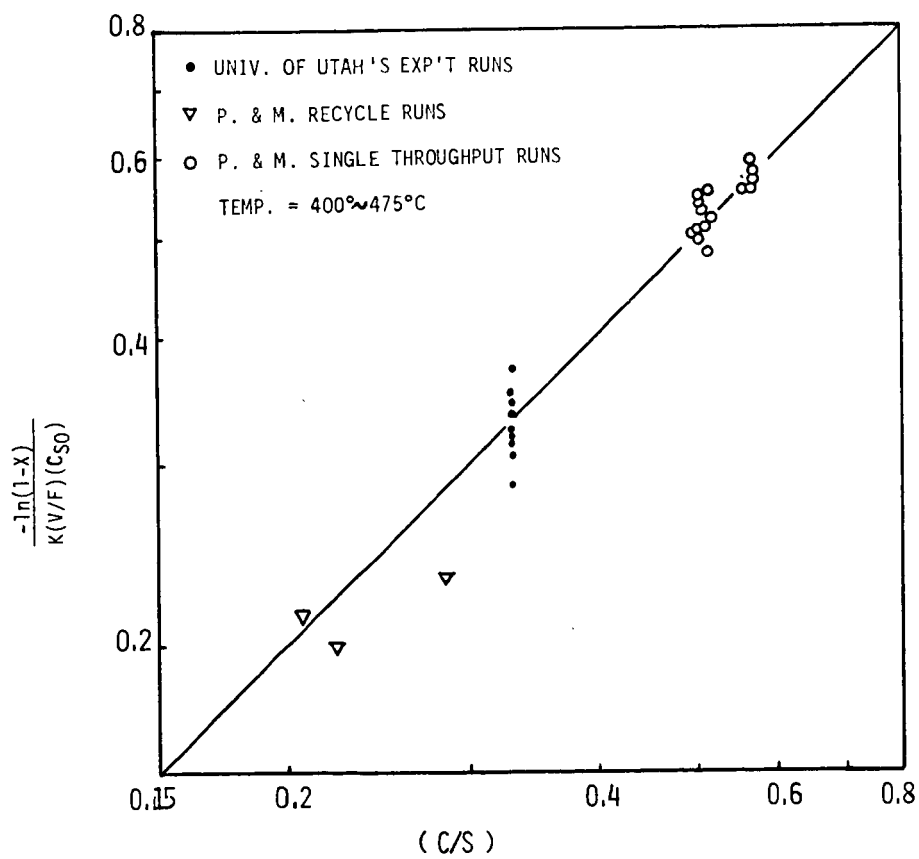Figure 9   COMPARISON OF CALCULATED AND EXPERIMENTAL CONVERSION ON SRC PROCESS.

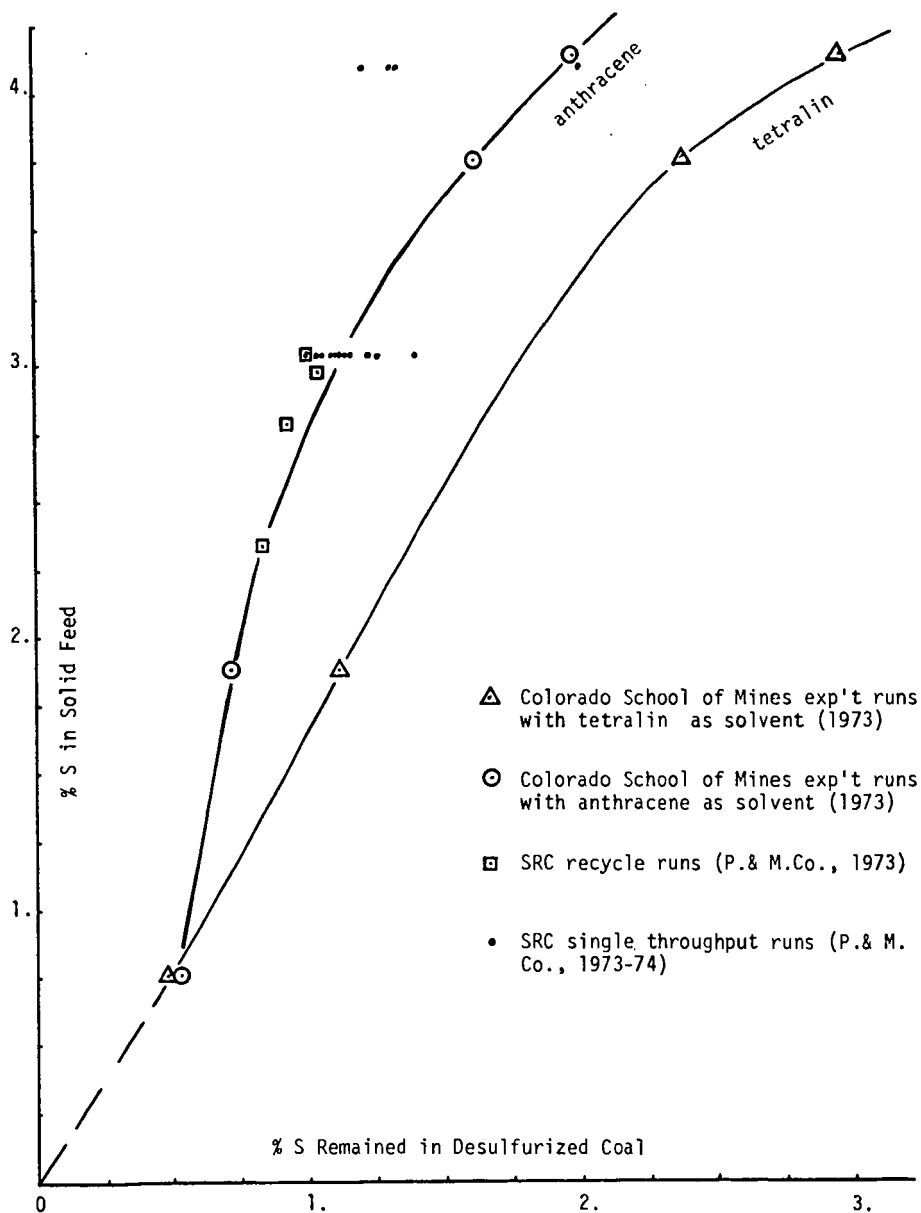Figure 10   EFFECT OF COAL TO SOLVENT RATIO ON COAL LIQUEFACTION.

Figure 11. ESTIMATION OF SULFUR LEVELS IN DESULFURIZED COAL.